

Supporting Information for

Synthesis of Fully Bio-based Polyesters from Plant Oil

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Esterification of Oleic Acid (Technical Grade)

Esterification of oleic acid was performed following the procedure reported by Jala's work¹. Oleic acid (10 g) was slowly added into a solution of 2% sulfuric acid in methanol (100 mL). The reaction mixture was refluxed for 6 hours and monitored by thin layer chromatography. After the reaction completed, the volatiles were evaporated under reduced pressure. The residue was dissolved in ethyl acetate, and washed with distilled water to remove the acid contents. The organic layer was dried using anhydrous sodium sulfate and the organic solvent was evaporated under vacuum. The silica gel column chromatography was used to purify the product components (9.4 g, 90% yield), where a mixture of hexane/ethyl acetate (97:3) was used as an eluent.

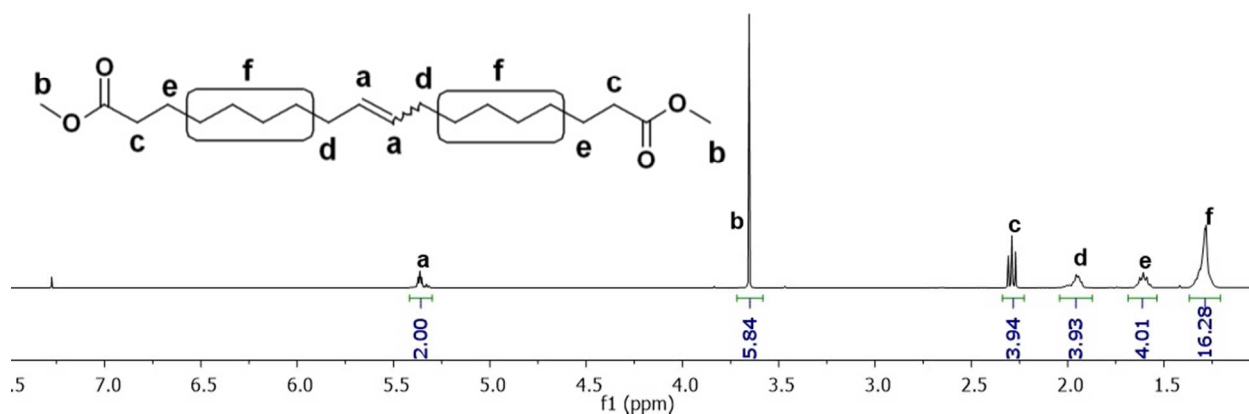
Synthesis of High Oleic Soybean Oil (or Canola Oil) Methyl Esters

Plant oil (100g) was taken into a round-bottom flask equipped with a stirring bar. A methanolic solution of KOH (1 g KOH in 25 mL methanol) was added into the reaction flask. The reaction mixture was stirred vigorously at 40 °C for 1.5 hours. The bottom layer (glycerol) was removed by pasteur pipette. The above procedure was repeated to ensure complete transesterification of triglycerides (oil). The reaction mixture was dissolved in 150 mL dichloromethane and washed firstly with distilled water (1 L) two times and then with 250 mL of saturated NaCl solution. The organic layer was dried over anhydrous sodium sulfate and solvent was evaporated. The crude product was purified with column chromatography using hexane/ethyl acetate (97:3) as mobile phase affording 85g FAMES.

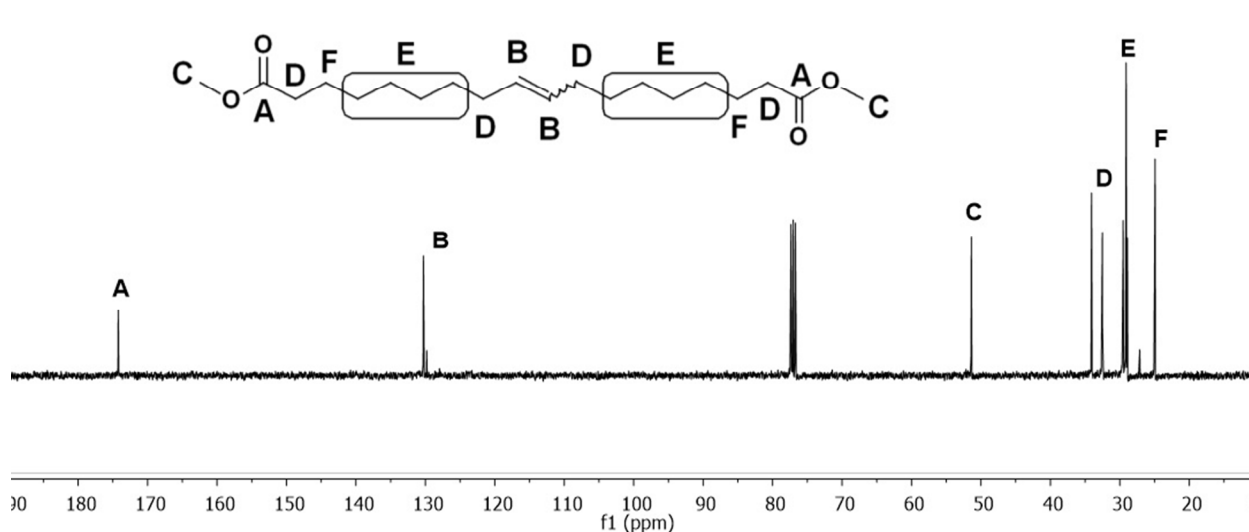
Charaterization of dimethyl-9-octadecene-1,18-dioate (diester):

¹H NMR (400 MHz, CDCl₃) δ 5.48 – 5.20 (m, 2H), 3.65 (s, 6H), 2.29 (t, *J* = 7.6 Hz, 4H), 2.27 – 1.81 (m, 4H), 1.68 – 1.50 (m, 4H), 1.45 – 1.22 (m, 16H). ¹³C NMR (101 MHz, CDCl₃) δ 174.23 (s), 130.28 (s), 129.80 (s), 51.37 (s), 34.07 (s), 32.52 (s), 29.58 (d, *J* = 12.8 Hz), 29.00 (d, *J* = 17.9 Hz), 27.14 (s), 24.92 (s). IR: 2924cm⁻¹, 2853cm⁻¹, 1737cm⁻¹ (C=O), 1435cm⁻¹, 1360cm⁻¹,

1 1244cm^{-1} (C-O-C ester), 1195cm^{-1} , 1168cm^{-1} (C-O-C ester), 968cm^{-1} , 880cm^{-1} , 725cm^{-1} . HRMS:
 2 m/z 340.2613.



3
 4 **Figure S1.** ^1H NMR spectrum (400MHz, CDCl_3) of dimethyl-9-octadecene-1,18-dioate.

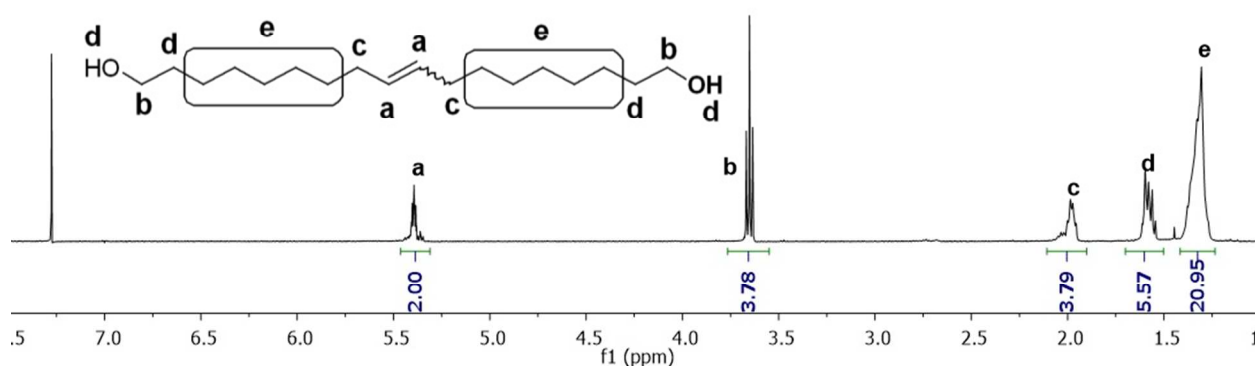


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 6 **Figure S2.** ^{13}C NMR spectrum (101MHz, CDCl_3) of dimethyl-9-octadecene-1,18-dioate.

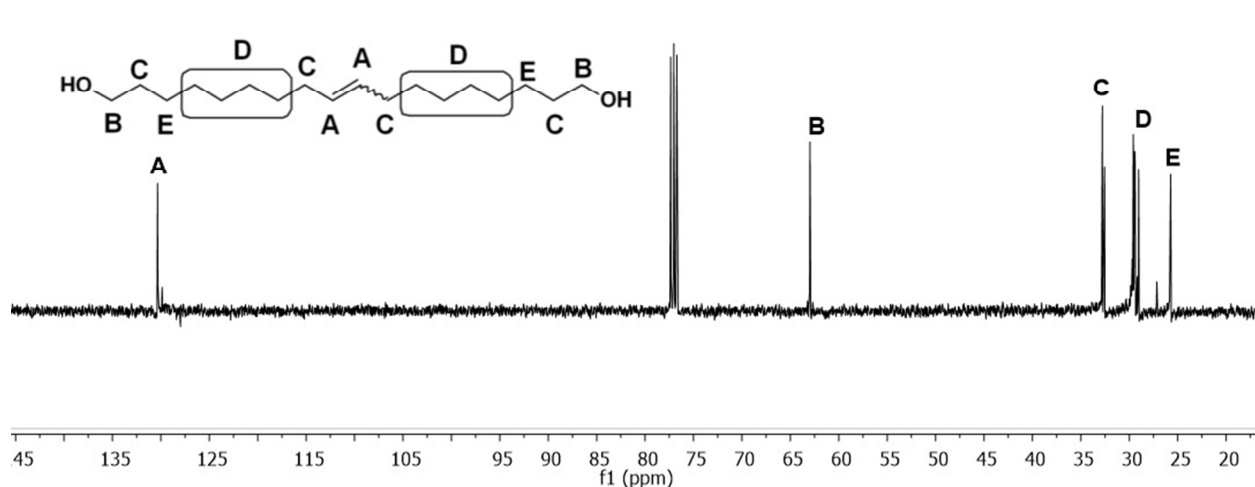
7 **Synthesis of 9-octadecene-1,18-diol**

8 The synthesis of 9-octadecene-1,18-diol (**diol**) was carried out following already reported
 9 method by Mecking². In a round bottom flask, LiAlH_4 (470 mg) was suspended in 40 mL dry
 10 THF and stirred vigorously. Dimethyl-9-octadecene-1,18-dioate (2 g) was dissolved in 20 mL
 11 dry THF in a separate vessel and added into suspension drop wise at room temperature. The
 12 slurry was refluxed for 1 hour and then stirred overnight at room temperature. After that, 0.5 mL
 13 distilled water, 0.5 mL 15% aqueous NaOH solution and another 0.5 mL distilled water were

1 added respectively to quench the reaction. The white precipitates were filtered off at 40°C, while
 2 the solvent was removed under reduced pressure to give white solid product. The crude product
 3 was dissolved in DCM and washed with distilled water, dried over anhydrous sodium sulphate.
 4 Solvent was evaporated under vacuum and the product was collected with 93% yield. ¹H NMR
 5 (400 MHz, CDCl₃) δ 5.56 – 5.22 (m, 2H), 3.65 (t, *J* = 6.6 Hz, 4H), 2.00 (dt, *J* = 10.9, 5.6 Hz,
 6 4H), 1.70 – 1.48 (m, 6H), 1.33 (dd, *J* = 16.8, 12.3 Hz, 20H). ¹³C NMR (101 MHz, CDCl₃) δ
 7 130.34 (s), 129.87 (s), 62.98 (s), 32.78 (s), 32.55 (s), 29.54 (dd, *J* = 21.7, 8.5 Hz), 29.12 (d, *J* =
 8 15.9 Hz), 27.16 (s), 25.73 (s). IR: 3340cm⁻¹(-OH), 2924cm⁻¹, 2853cm⁻¹, 1461 cm⁻¹, 1055cm⁻¹,
 9 968cm⁻¹. HRMS: m/z 284.2715.



10
 11 **Figure S3.** ¹H NMR spectrum (400MHz, CDCl₃) of 9-octadecene-1,18-diol.



13
 14 **Figure S4.** ¹³C NMR spectrum (101MHz, CDCl₃) of 9-octadecene-1,18-diol.

Nuclear Magnetic Resonance (NMR) Results of Polyester.

^1H NMR (400 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$) δ 5.37 (d, $J = 14.4$ Hz, 4H), 4.03 (t, $J = 6.6$ Hz, 4H), 2.28 (t, $J = 7.4$ Hz, 4H), 2.04 (d, $J = 62.5$ Hz, 8H), 1.56 (t, $J = 23.9$ Hz, 8H), 1.29 (s, 36H). ^{13}C NMR (101 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$) δ 173.86 (s), 130.16 (s), 129.78 (s), 64.27 (s), 34.23 (s), 32.47 (s), 29.20 (dt, $J = 23.2, 7.6$ Hz), 28.51 (s), 27.08 (s), 25.80 (s), 24.87 (s). IR: 2918cm^{-1} , 2850cm^{-1} , 1733cm^{-1} ($\text{C}=\text{O}$), 1466cm^{-1} , 1242cm^{-1} ($\text{C}-\text{O}-\text{C}$ ester), 1169cm^{-1} ($\text{C}-\text{O}-\text{C}$ ester), 963cm^{-1} , 722cm^{-1} .

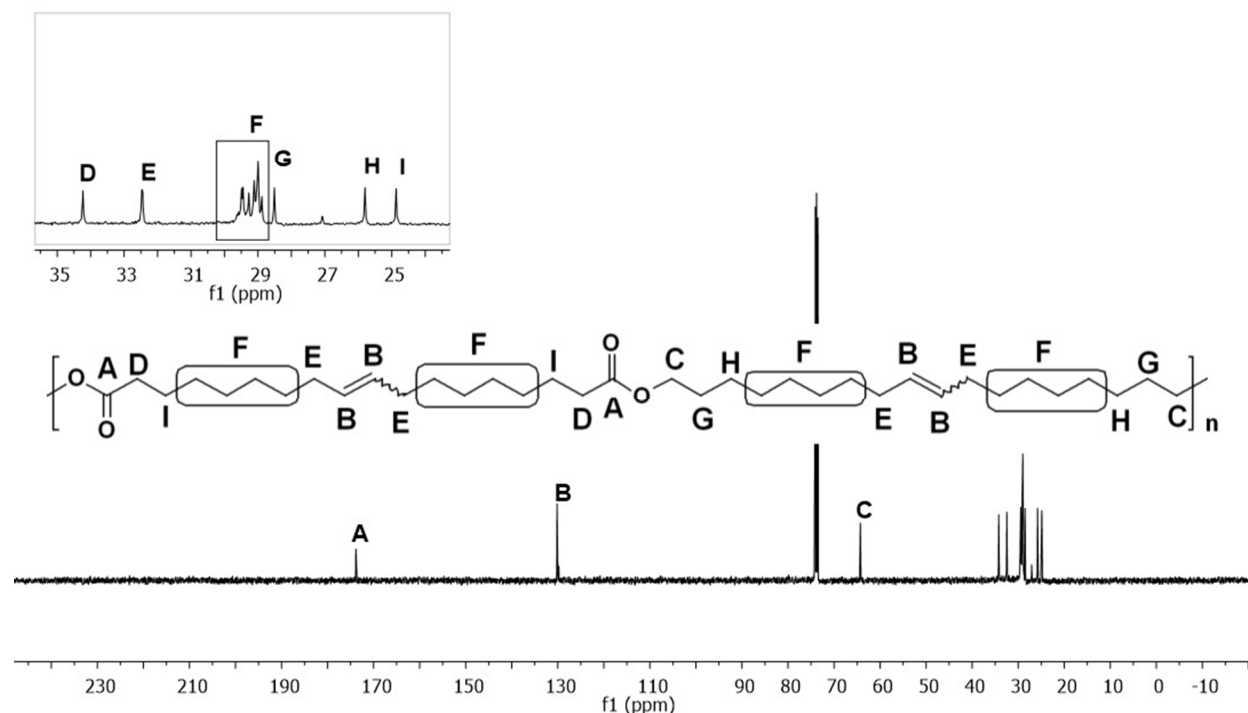


Figure S5. ^{13}C NMR spectrum (101MHz, $\text{C}_2\text{D}_2\text{Cl}_4$) of polyester (entry 2, table 4).

Calibration of Standards by GC-FID

Highly pure methyl oleate and diester were dissolved in DCM for the preparation of standard solutions with different concentrations. Values of their peak areas were used to plot standard curves and to calculate mass response factors. The concentrations of FAMES and diester from self-metathesis were calculated using their mass response factors.

1 Data and Characterizations

2 GC-MS:

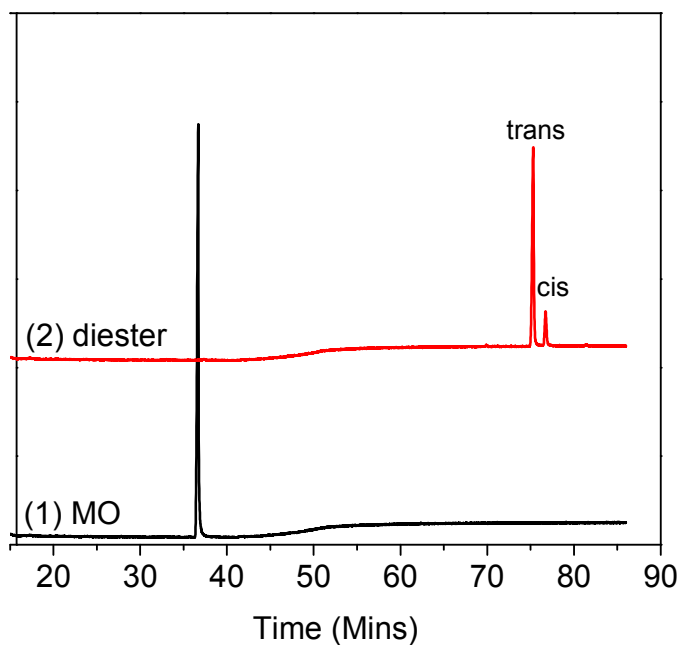


Figure S6. GC-MS spectra of pure methyl oleate (MO) and diester.

5 GC-FID Calibration:

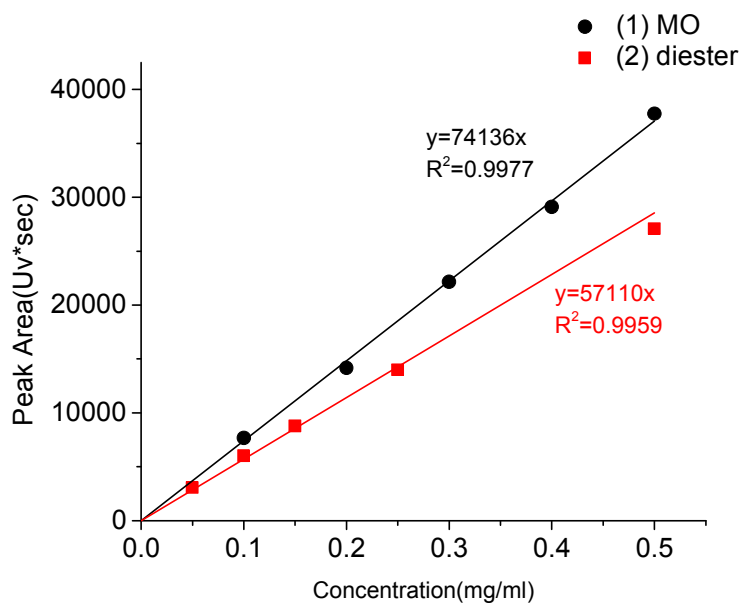


Figure S7. Linear fitting curves of methyl oleate (MO) and diester standards.

Equilibrium State Determination of Self-metathesis Reactions:

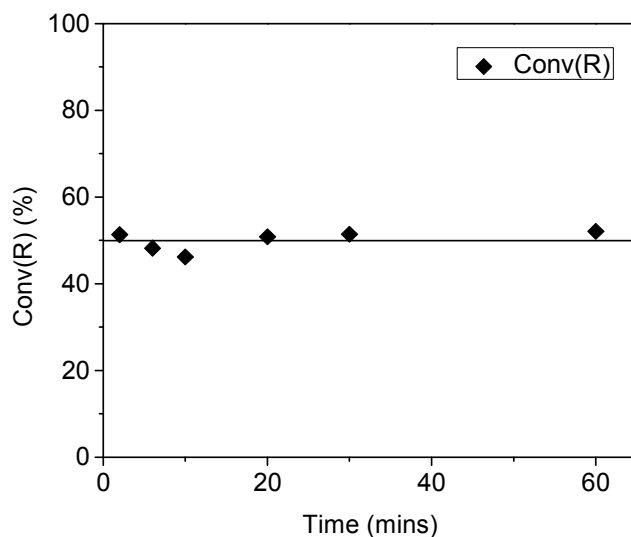


Figure S8. Conv(R) of FAMES after self-metathesis with 0.05 mol% **HG2** catalyst at 50°C with different time intervals.

Polycondensation by Conventional Heating using $\text{Ti}(\text{OBu})_4$ as Catalyst :

Table S1. Polycondensation of diester and diol by conventional heating using $\text{Ti}(\text{OBu})_4$ catalyst

Entry	Catalyst	Time (h)	T_m (°C)	ΔH_m (J/g)
1	2% $\text{Ti}(\text{OBu})_4$	8	50.6	87.5
2	2% $\text{Ti}(\text{OBu})_4$	16	49.8	78.9

Polyesters Images under Different Pressures using Microwave Technology:

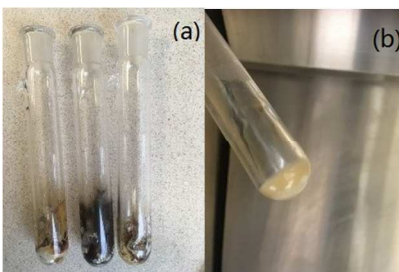
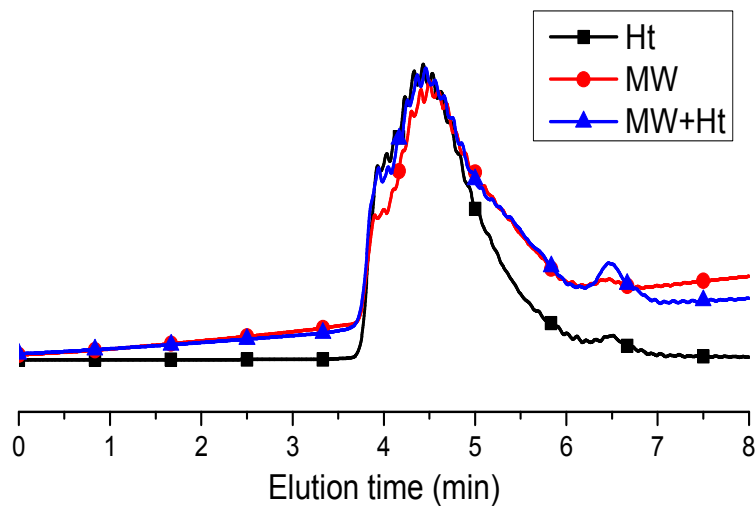


Figure S9. (a) The charred material and broken vessel under microwave conditions connected to high vacuum (~ 0.1 bar), (b) polyester obtained using microwave conditions (200 °C) under nitrogen atmosphere for 15 min.

1 GPC:



2
3 **Figure S10.** Gel permeation chromatography (GPC) traces of polyesters from conventional
4 heating (Ht), microwave heating (MW) and coupled heating methods (MW + Ht).

5 **Appearance of Polyester Films:**



7
8 **Figure S11.** Films of polyester prepared by heating (left) and coupled methods (right).

1 DMA:

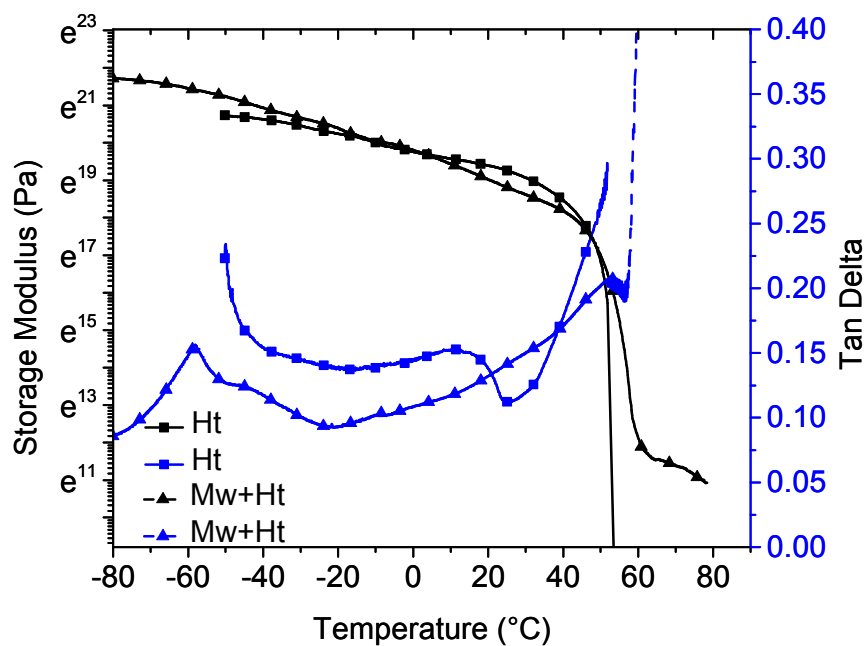


Figure S12. Storage modulus (black) and tan delta (blue) curves of polyesters by conventional heating (Ht) and by coupled methods (MW+ Ht).

5 Mechanical Tests:

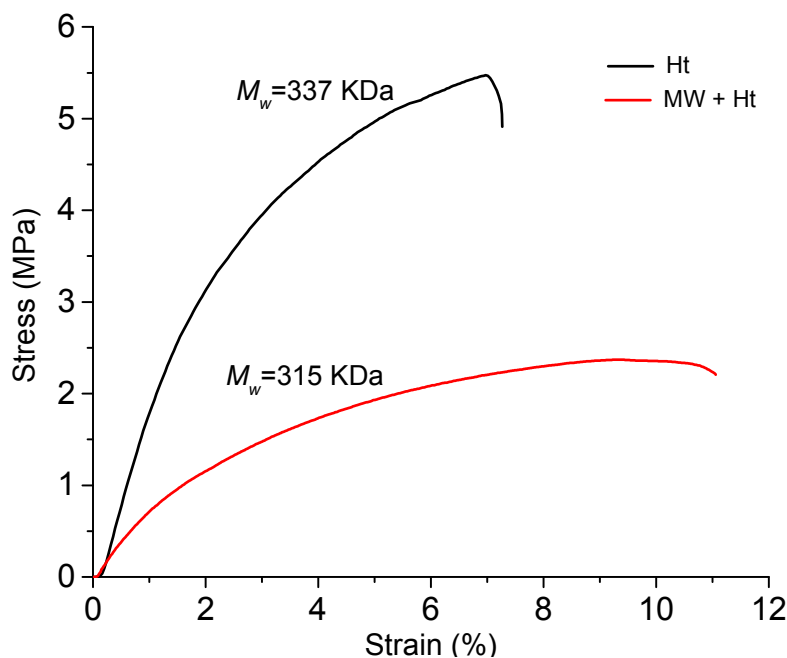


Figure S13. Mechanical tests of polyesters obtained by conventional heating (Ht) and by coupled method (MW+ Ht).

References

1. Srikanth, V.; Prasad, R.; Poornachandra, Y.; Babu, V. P.; Kumar, C. G.; Jagadeesh, B.; Jala, R. C. R., Synthesis of dihydrosterculic acid-based monoglucosyl diacylglycerol and its analogues and their biological evaluation. *Eur. J. Med. Chem.* **2016**, *109*, 134-145. doi: 10.1016/j.ejmech.2015.12.048.
2. Quinzler, D.; Mecking, S., Linear semicrystalline polyesters from fatty acids by complete feedstock molecule utilization. *Angew. Chem. Int. Ed.* **2010**, *49* (25), 4306-4308. doi: 10.1002/ange.201001510.